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A STUDY OF THE HYDROGEN-DEUTERIUM EXCHANGE IN
THE HETEROGENEOUS PHASE THROUGH ION EXCHANGE

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by Piroska Csanyi Fodorne

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A STUDY OF THE HYDROGEN-DEUTERIUM EXCHANGE IN
THE HETEROGENEOUS PHASE THROUGH ION EXCHANGES

[Following is a translation of an article by Piroška Csanyi Fodorne in Magyar Kémiai Folyóirat (Hungarian Chemical Periodical), Vol LXIV, No 11, Budapest, 1958, pages 417-428.]

I. Cation Exchange

Isotope exchange reactions are chemical processes in which a macroscopic change takes place in two or more molecular types containing atoms of the same element as a result of isotope-distribution atomic exchanges. Because the isotopes are chemically identical the thermal effects connected with these processes are negligably small ($\Delta H \approx 0$); thus the free enthalpia drop accompanying such an automatic process essentially is caused by the increase in configurational entropy:

$$\Delta G = - T \Delta S$$

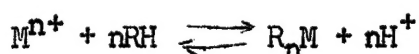
Many exchange reactions between hydrogen and deuterium atoms in a heterogeneous system are known. For example, exchange occurs between deuterium oxide and the carboxyl hydrogen atoms of sulphuric acid, acetic acid, and succinic acid, and the hydroxyl hydrogen atoms of sodium hydroxide, sucrose, ethanol, phenol and hydroquinone.¹ [IUS Atomic Energy Commission NBS-4611, 1956, page 80; NBS-4674, 1956, page 25, NBS-4712, 1956, page 18.] Exchange experiments have shown that those hydrogen atoms may be exchanged directly with deuterium which have ionic bonds, or the bonds of which may form ionic bonds (such as in the case of keto-enol tautomerism). The exchange of hydrogen atoms in covalent bonds is very slow, or does not occur at all.

An interesting instance of the hydrogen-deuterium exchange reaction is the exchange which occurs in the heterogeneous phase, because investigation of this exchange may provide valuable information on the heterogeneous system.

We intended to utilize the hydrogen-deuterium exchange between ion-exchange resin and deuterium oxide for the purpose of investigation of the ion exchange mechanism and for the performance of preliminary studies of reactions catalyzed by ion-exchangers, using deuterium and tritium indicators. Without a doubt direct exchange between the resin and water plays a role in the latter reaction to the extent that separate acknowledgement of this partial process appears absolutely necessary.

Ion-exchange resins are synthetic polymers consisting of network layers held together by cross-bonds, and containing active exchange groups (phenolic, sulphonic acid or carboxylic groups).

The layered structure makes them pervious with respect to solution, and the cross-bonds provide mechanical strength and insolubility. When the resin comes in contact with an aqueous solution it absorbs water, thus the cations of the solution may diffuse into the pores and the acidic hydrogen of the active groups may exchange with other cations. The exchange reaction may be represented by the following equation:



M^{n+} represents the cation in solution, and R represents the insoluble anionic portion of the resin. Exchange reactions reach equilibrium slowly because the diffusion of the ions toward and away from the acid groups is a slow process. The activity of a resin with respect to various ions increases with an increase in the ion saturation, and decreases with an increase in the radius of the hydrated ion.² [2 O. Samuelson: Ion Exchangers in Analytical Chemistry, John Wiley Sons, New York, 1952, page 35.] According to decreasing activity, we have: $Th^{4+} > La^{3+} > Ba^{2+} > Cs^+$, or $Cs^+ > Rb^+ > K^+ > Na^+ > H^+ > Li^+$.

Experiments

The exchange of acidic hydrogen atoms of cation exchangers were investigated in an aqueous solution of deuterium oxide. The following cation-exchanger resins were studied: Amberlite IR-120 and Amberlite IRC-50. The significant data of the resins are shown in Table 1.³ [3 F. C. Nachod and J. Schubert: Ion Exchange Technology, Academic Press, Inc. Publishers, New York, 1956, page 24.]

TABLE 1

Significant Data of Resins

| Name | Composition | Manu- fact- urer's Spec- ifica- tion of Capacity mckv/g | Experimental Capacity, mckv/g | Total Capacity, mckv/g | High- est Util- izable Temp- erature * | Useable Range, in PH |
|---------------------|---------------------------------|--|----------------------------------|---------------------------|--|-------------------------------|
| Amberlite IR-120 | Sulphonic Acid Polystyrol | 4.9-5.0 | 4.2 4.2 | 4.2 4.2 | 121 C° | 0-14 |
| Amberlite IRC-50 | Carboxylic, Polyacrylic Acid | 10.0 | 10.0 10.0 | 9.2 8.1 | 121 C° | 7-14 |

*Temperature refers to the sodium salt of the resin.

The exchange reactions were allowed to proceed under static conditions, using the same mass ratio of resin to deuterium oxide. The resins were pulverized and divided into three size fractions with series-sifting: 0.6 to 0.45 mm, 0.4 to 0.35 mm, and 0.1 to 0.06 mm. The separated fractions then were activated with 10 percent sulphuric acid for two hours, to remove any cations which may be present. After washing to remove sulphate ions the resin was dried in air. Each resin portion was used only once. A 2-gram sample of each air-dry fraction was weighed out, shaken for the desired length of time with 50 g deuterium oxide aqueous solution, the resin was filtered and the change in deuterium oxide concentration in the residue was determined. In the experiments described in the present report the starting concentration of deuterium in the solution was 11.392 mol-% in all cases (the results of a series of tests with higher concentrations will be reported later), which showed a change of several hundredths of a percent, at the most, during the course of the exchange (Tables 2 to 5). Thus the exchanges took place in a medium of practically constant concentration, but the changes still were sufficiently large to ensure adequate measuremental accuracy (see below).

TABLE 2

Exchange Capacity as a Function of Type of Resin
 Starting concentration of solution 11.392±0.0005 mol-% D₂(Y₀);
 71.5 C°; 2 g resin + 50 g solution; p_H = 6.0; r₀ = 0.6
 to 0.45 mm grain size
 A = Amberlite IR-120 B = Amberlite IRC-50

| Agitation Time | Decrease in Solution Con- centration, $\Delta Y \pm 0.5$ | | Decrease in Deuterium Content of Solution (ΔY) mol- %±0.0005 | | Quantity of Deuterium Bound on the Resin (m_D) mckv/g | | $X_D = \frac{m_D}{m_H} X_D^0 = \frac{m_D}{m_H}$ | | |
|-------------------|---|------|---|--------|--|-------|---|--------|--------|
| | A | B | A | B | A | B | A | B | A |
| 1 hour | 7.9 | 11.1 | 0.0074 | 0.0103 | 0.202 | 0.282 | 0.048 | 0.0282 | 0.0161 |
| 2 " | 15.1 | 21.7 | 0.0140 | 0.0201 | 0.384 | 0.551 | 0.091 | 0.0551 | 0.0304 |
| 3 " | 17.9 | 23.6 | 0.0166 | 0.0219 | 0.455 | 0.600 | 0.108 | 0.0600 | 0.0361 |
| 4 " | 17.8 | 25.1 | 0.0165 | 0.0233 | 0.452 | 0.639 | 0.107 | 0.0639 | 0.0359 |
| 6 " | 18.0 | 25.6 | 0.0167 | 0.0237 | 0.458 | 0.650 | 0.109 | 0.0650 | 0.0363 |

TABLE 2 (right side)

| | a | | a ² |
|---------|-------|-------|----------------|
| | A | B | A |
| 6 hours | 0.953 | 0.542 | 0.293 |

TABLE 3

Exchanger Capacity as a Function of Temperature
 Starting concentration of solution 11.392±0.0005 mol-% $D_2(Y_0)$;
 2 g resin + 50 g solution; $P_H = 6.0$; $r_0 = 0.6$ to 0.45 mm

(a) Amberlite IR-120

| Agitation Time | Decrease in Solution Concentration, $\Delta Y \pm 0.5$ | | Decrease in Deuterium Concentration of Solution, $\Delta Y \pm 0.0005$ | | Quantity of Deuterium Bound on the Resin, $(m_D)_{mckv/g}$ | | $X_D = \frac{m_D}{m_H}$ | | $X_D^* = \frac{m_D}{3m_H}$ | | a | | a' |
|----------------|--|---------|--|--------|--|-------|-------------------------|--------|----------------------------|--------|---------|-------|-------------|
| | 20 Co | 71.5 Co | 71.5 Co | 90 Co | 71.5 Co | 90 Co | 71.5 Co | 90 Co | 71.5 Co | 90 Co | 71.5 Co | 90 Co | |
| 30 min | 13.0 | 13.0 | 0.0120 | 0.0120 | 0.329 | 0.329 | 0.0783 | 0.0783 | 0.0261 | 0.0261 | | | |
| 1 hour | 7.9 | 17.0 | 0.0074 | 0.0166 | 0.155 | 0.202 | 0.048 | 0.108 | 0.0161 | 0.0361 | | | |
| 2 " | 15.1 | 23.2 | 0.0110 | 0.0215 | 0.589 | 0.384 | 0.091 | 0.140 | 0.0304 | 0.0468 | | | |
| 3 " | 17.9 | 22.4 | 0.0166 | 0.0208 | 0.570 | 0.455 | 0.108 | 0.135 | 0.0361 | 0.0452 | | | |
| 4 " | 17.8 | 22.7 | 0.0165 | 0.0210 | 0.576 | 0.452 | 0.107 | 0.137 | 0.0359 | 0.0457 | | | |
| 6 " | 18.0 | 23.0 | 0.0167 | 0.0213 | 0.584 | 0.458 | 0.109 | 0.139 | 0.0363 | 0.0463 | 0.953 | 1.258 | 0.293 0.378 |
| | 60Co | 80Co | 60Co | 80Co | 80Co | 60Co | 60Co | 80Co | 60Co | 80Co | 60Co | 80Co | 60Co 80Co |
| 6 hours | 14.9 | 20.9 | 0.0138 | 0.0194 | 0.532 | 0.257 | 0.061 | 0.126 | 0.0204 | 0.0424 | 0.507 | 1.129 | 0.162 0.345 |

TABLE 3 (continued)

(b) Amberlite IRC-50

(Left side)

| Agitation Time | Decrease in Solution Concentration, $\Delta Y \pm 0.5$ | | | Decrease in Deuterium Concentration (ΔY) mol-% ± 0.0005 | | | Quantity of Deuterium Bound on the Resin (mD) mckv/g | | |
|----------------|--|---------|-------|---|---------|--------|--|---------|-------|
| | 20 Co | 71.5 Co | 90 Co | 20 Co | 71.5 Co | 90 Co | 20 Co | 71.5 Co | 90 Co |
| 1 hour | 0 | 11.1 | 13.1 | 0 | 0.0103 | 0.0121 | 0 | 0.282 | 0.334 |
| 2 " | 0 | 21.7 | 18.7 | 0 | 0.0201 | 0.0173 | 0 | 0.551 | 0.474 |
| 3 " | 0 | 23.6 | 21.0 | 0 | 0.0219 | 0.0195 | 0 | 0.600 | 0.534 |
| 4 " | 0 | 25.1 | 21.8 | 0 | 0.0233 | 0.0202 | 0 | 0.639 | 0.554 |
| 6 " | 0 | 25.6 | 21.8 | 0 | 0.0237 | 0.0202 | 0 | 0.650 | 0.554 |
| | | | | | 60 Co | 80 Co | | 60 Co | 80 Co |
| 6 hours | | 15.6 | 24.5 | | 0.0115 | 0.0227 | | 0.397 | 0.622 |

TABLE 3 (continued)

(b) Amberlite IRC-50

(Right side)

| $X_D \approx \frac{m_D}{m_H}$ | | $X_{Dt} = \frac{m_H}{m_{Ht}}$ | | a | | a' | |
|-------------------------------|--------|-------------------------------|--------|--------|-------|-------|-------|
| 20 | Co | 71.5 | Co | 20 | Co | 90 | Co |
| 0 | 0.0282 | 0.0334 | 0.0282 | 0.0412 | | | |
| 0 | 0.0551 | 0.0474 | 0.0551 | 0.0585 | | | |
| 0 | 0.0600 | 0.0534 | 0.0600 | 0.0660 | | | |
| 0 | 0.0639 | 0.0554 | 0.0639 | 0.0683 | | | |
| 0 | 0.0650 | 0.0554 | 0.0650 | 0.0683 | 0 | 0.542 | 0.457 |
| | | | | | | 0.572 | |
| 60 | Co | 80 | Co | 60 | Co | 80 | Co |
| 0.0397 | 0.0622 | 0.0397 | 0.0676 | 0.322 | 0.517 | 566.0 | |

TABLE 4

Exchange Capacity as a Function of P_H (HCl) of
 Solution Starting concentration of solution 11.392±0.0005 mol-% $D_2(Y_0)$;
 2 g resin + 50 g solution; 71.5°C; $r_0 = 0.6$ to 0.45 mm

(a) Amberlite IR-120

| Agitation Time | Decrease in Solution Concentration, $\Delta Y \pm 0.5$ | | Decrease in Deuterium Content of Solution, $(\Delta Y) \pm 0.0005$ | | Quantity of Deuterium Bound on the Resin (m_D) | | $X_D = \frac{m_D}{m_H}$ | | $X_D^2 = \frac{m_D^2}{3m_H}$ | | a | | a' | |
|----------------|--|-----------|--|-----------|--|-----------|-------------------------|-----------|------------------------------|-----------|-----------|-----------|-----------|-----------|
| | P_H 6.0 | P_H 2.2 | P_H 6.0 | P_H 2.2 | P_H 6.0 | P_H 2.2 | P_H 6.0 | P_H 2.2 | P_H 6.0 | P_H 2.2 | P_H 6.0 | P_H 2.2 | P_H 6.0 | P_H 2.2 |
| 30 min | --- | 11.8 | --- | 0.0109 | --- | 0.298 | --- | 0.071 | --- | 0.0237 | --- | --- | --- | --- |
| 1 hour | 7.9 | 17.9 | 0.0074 | 0.0166 | 0.202 | 0.455 | 0.048 | 0.108 | 0.0161 | 0.0361 | --- | --- | --- | --- |
| 2 hours | 15.1 | 22.4 | 0.0140 | 0.0208 | 0.384 | 0.570 | 0.091 | 0.135 | 0.0304 | 0.0452 | --- | --- | --- | --- |
| 3 hours | 17.9 | 23.3 | 0.0166 | 0.0216 | 0.455 | 0.592 | 0.108 | 0.140 | 0.0361 | 0.0468 | --- | --- | --- | --- |
| 4 hours | 17.8 | 22.9 | 0.0165 | 0.0212 | 0.452 | 0.581 | 1.09 | 0.138 | 0.0359 | 0.0461 | --- | --- | --- | --- |
| 6 hours | 18.0 | 23.6 | 0.0167 | 0.0219 | 0.458 | 0.600 | 1.07 | 0.143 | 0.0363 | 0.0476 | 0.953 | 1.301 | 0.293 | 0.390 |
| 6 hours | | | | | | | | | | | | | | |
| | P_H 4.0 | P_H 1.0 | P_H 4.0 | P_H 1.0 | P_H 4.0 | P_H 1.0 | P_H 4.0 | P_H 1.0 | P_H 4.0 | P_H 1.0 | P_H 4.0 | P_H 1.0 | P_H 4.0 | P_H 1.0 |
| | 22.0 | 24.0 | 0.0204 | 0.0223 | 0.559 | 0.611 | 0.133 | 0.145 | 0.0444 | 0.0485 | 1.197 | 1.329 | 0.362 | 0.397 |

TABLE 4 (continued)

(b) Amberlite IRC-50

| Agitation Time | Decrease in Solution Concentration, $\Delta Y \pm 0.5$ | Decrease in Deuterium Concentration (ΔY) mol-% | | Quantity of Deuterium Bound on the Resin (m_D) mckv/g | | $X_D = \frac{m_D}{m_H}$ | | a |
|----------------|--|--|--------|---|--------|-------------------------|--------|-------------|
| | | PH 6.0 | PH 2.2 | PH 6.0 | PH 2.2 | PH 6.0 | PH 2.2 | |
| 1 hour | 11.1 | 0.0103 | 0.0074 | 0.282 | 0.203 | 0.0282 | 0.0203 | |
| 2 " | 21.7 | 0.0201 | 0.0103 | 0.551 | 0.282 | 0.0551 | 0.0282 | |
| 3 " | 23.6 | 0.0219 | 0.0120 | 0.600 | 0.329 | 0.0600 | 0.0329 | |
| 4 " | 25.1 | 0.0233 | 0.0114 | 0.639 | 0.312 | 0.0639 | 0.0312 | |
| 6 " | 25.6 | 0.0237 | 0.0120 | 0.650 | 0.329 | 0.0650 | 0.0329 | 0.542 0.261 |
| | | PH 4.0 | PH 5.0 | PH 4.0 | PH 5.0 | PH 4.0 | PH 5.0 | |
| | 16.3 | 0.0151 | 0.0179 | 0.414 | 0.490 | 0.0414 | 0.0490 | 0.336 0.402 |
| 6 hours | | | | | | | | |

TABLE 5 (continued)

(b) Amberlite IRS-50

| Agitation Time | Decrease in Solution Concentration, $\Delta Y \pm 0.5$ | | Decrease in Deuterium Content of Solution (ΔY) mol-% ± 0.0005 | | Quantity of Deuterium Bound on the Resin (m_D) mckv/g | | $X_D = \frac{m_D}{m_H}$ | | a |
|----------------|--|--------|---|--------|---|--------|-------------------------|--------|-------------|
| | PH 6.0 | PH 2.1 | PH 6.0 | PH 2.1 | PH 6.0 | PH 2.1 | PH 6.0 | PH 2.1 | |
| 1 hour | 11.1 | 5.8 | 0.0103 | 0.0054 | 0.282 | 0.148 | 0.0282 | 0.0148 | |
| 2 " | 21.7 | 8.2 | 0.0201 | 0.0075 | 0.551 | 0.207 | 0.0551 | 0.0207 | |
| 3 " | 23.6 | 8.6 | 0.0219 | 0.0079 | 0.600 | 0.217 | 0.0600 | 0.0217 | |
| 4 " | 25.1 | 8.2 | 0.0233 | 0.0075 | 0.639 | 0.207 | 0.0639 | 0.0207 | |
| 6 " | 25.6 | 8.6 | 0.0237 | 0.0079 | 0.650 | 0.217 | 0.0650 | 0.0217 | 0.542 0.173 |
| 6 hours | PH 4.1 | PH 1.0 | PH 4.1 | PH 1.0 | PH 4.1 | PH 1.0 | PH 4.1 | PH 1.0 | |
| | 14.9 | 3.9 | 0.0138 | 0.0036 | 0.378 | 0.0987 | 0.0378 | 0.0987 | 0.306 0.077 |

The exchange capacity of the resins were investigated as a function of the temperature (60, 71.5, 80 and 90 C°), the pH of the solution (1.0 to 6.0), and the grain size of the resin ($r_0 = 0.6$ to 0.45 mm, 0.4 to 0.35, and 0.1 to 0.06 mm radius fractions). The exchange occurring in the 11.392 mol-% starting solution was taken as the standard at 71.5 C°, pH 6.0 and with the 0.6 to 0.45mm radius fraction. (The pH 6 level derives from carbon dioxide dissolved in distilled water.)

Determination of the speed of absorption of deuterium by the resin and of the end value, which were the goal of the experiment, theoretically are attainable in two ways:

(a) the direct method, according to which the deuterium content of the resin and solution are determined separately at given points of time, or

(b) the indirect method, according to which the deuterium concentration of the solution only is determined before and after exchange, or at the extreme phases of the process. The quantity of deuterium which has migrated to the resin may be calculated from the difference between the two concentrations. Because the direct method would have been very difficult in our experiments (the water produced during burning away of the resin would have had to be analyzed), the deuterium absorption by the resin was traced through measurement of the concentration of deuterium in solution.

Determination of the Deuterium Content

The deuterium content of the water was determined by concentration measurement based on the familiar suspension method at 25 degrees Centigrade, with 0.005 C° accuracy.⁴ [4 K. Cziike and P. F. Csanyi: Magy. Kem. Folyoirat (Magyar Kemiai Folyoirat -- Hungarian Chemical Journal), No 61, 1955, page 385.] The suspension material used in the concentration measurements was selected to be suspended in deuterium oxide solution of the starting concentration level used in the experiments, at 25 C°. The D₂O mol-% may be calculated from the concentration by the following method.⁵ [5 I. Kirshenbaum: Physical Properties and Analysis of Heavy Water, McGraw-Hill Book Company, Inc., New York, 1951, page 14.]

Assuming that in H₂O - D₂O mixtures the molecular volumes (V_1 and V_2) are additive, for the sample concentration of D₂O in an N molecular fraction may be written as follows (M_1 and M_2 are molecular weights):

$$d = \frac{(1-N) M_1 + NM_2}{(1-N) V_1 + NV_2}$$

If the concentration of pure H₂O (deuterium oxide-free water) is d_1 and the D₂O concentration is d_2 , then:

$$V_1 = \frac{M_1}{d_1} \quad \text{and} \quad V_2 = \frac{M_2}{d_2}$$

Substituting these values and solving the equation for N, after the appropriate manipulations we arrive at the following expression:

$$N = \frac{a \Delta d}{1 - b \Delta d}$$

where

$$d = d = d_1 \quad a = \frac{M_1 d_2}{M_2 d_1 (d_2 - d_1)} \quad b = \frac{1 - \frac{M_1 d_2}{M_2 d_1}}{d_2 - d_1}$$

The numerical values to be substituted are: $M_1 = 18.01571$ and $M_2 = 20.02836$; at 25 °C: $d_1 = 0.99706$ g/ml (protium oxide is $16 \cdot 10^{-6}$ density units lighter than normal water) and $d_2 = 1.10451$ g/ml. Thus:

$$a = 9.2735 \text{ and } b = 0.0329$$

or expressing the deuterium content in mol percentage (Y) instead of mol fraction:

$$Y = \frac{927.35 \Delta d}{1 - 0.0329 \Delta d} \quad (1)$$

In our experiments the 11.392 mol-% solution was the standard, and the concentration changes which took place with respect to this value are presented in the customary Y - units ($1 Y = 10^{-6}$ density units). Because the reduction in concentration of deuterium oxide solution (reduction in density) as a result of exchange is only a few hundredths of one mol percent (several hundred-thousandths of a density unit), the second member of the numerator in equation (1) is negligible with respect to unity. According to the above the appropriate changes in mol numbers are as follows:

$$\Delta Y = 9.2735 \cdot 10^{-4} \Delta Y$$

The solutions were prepared for determinations by alkylizing the organic materials dissolved out of the resin by boiling with $KMnO_4$, and then distilling twice. The deuterium content of the main solution was determined by this method also.

In the case of hydrochloric acid and sulphuric acid solutions, because exchange takes place between the acids and the deuterium oxide, it is essential that the hydrogen atoms of the hydrochloric and sulphuric acids also are included in the solution to be determined. Because of this the solutions were exposed to dessicated magnesium carbonate and distilled until dry. All data are the averages of three parallel experiments.

Determination of the Total Exchange Capacity of the Resin

The total ion-exchange capacity of the resins was determined by the addition of more $n/10$ NaOH solution than the manufacturer's specification of capacity at the given temperature. Allowing a sufficient time for the hydrogen atoms of the cation exchangers to be exchanged with sodium ions, the resin sample was filtered and thoroughly washed with distilled water, and the excess alkali remaining in solution was back-titrated with $n/10$ HCl. The quantity of Na ions bound by the resin, related to the weight unit, is the capacity of the resin (m_H), which it is customary to express in milliequivalents (mekv/g) (multiplication of the equivalent value by the Avogadro number gives the number of active places of the resin).¹¹ [11 W. F. Libby: J. Chem. Phys., No 11, 1943, page 101.]

Hydrogen-Deuterium Exchange Capacity as a Function of the Active Groups of the Resin

Comparison of the H-D exchange capacity of the two cation exchangers under standard conditions (Table 2, Figure 1) shows that the exchange capacity of Amberlite IRS-50 is greater than that of Amberlite IR-120. However, when the quantity of deuterium bound on the resin (m_D) is converted to unit ion exchange capacity, the above order is changed, and the deuterium mol fraction

$$X_D = \frac{m_D}{m_H}$$

of IRC-50 is smaller than that of Amberlite IR-120. The reason for this probably is the fact that although sulphonic acid resins form a completely dissociated internal solution, according to the neutralization curve dissociation is very slight in the carboxylic resin, similar to the case of small-molecular, weak acids.⁶ [6 R. Griessbach: Austauschadsorption in Theorie und Praxis (Exchange Adsorption in Theory and Practice), Akademie-Verlag, Berlin, 1957, page 278.]

Comparison of the exchange speed shows that the speed of exchange on the sulphonic acid resin is greater than on the carboxylic resin. Amberlite IR-120 reaches its end value in three hours, while it takes Amberlite IRC-50 four hours to reach the end point.

The H-D Exchange Capacity as a Function of Temperature

Temperature generally has a small effect upon the end values of ion exchange, with exceptions to this rule in the case of neutralization reactions. The effect of temperature depends upon the change which occurs in the dissociation of the solutions and in the swollen condition of the exchanger. As a result of these two effects the quantity of exchanged ions may increase with an increase in temperature. If active groups are split off from the resin with an increase in temperature, an increase in temperature has an opposite effect upon the exchange.

Temperature has a significant effect upon the speed of exchange if the process requires thermal activation, or if diffusion is the speed-determining step in respect to the chemical reaction of exchange.

At 20 C° there is no measurable exchange between the investigated cation exchangers and deuterium oxide, and this occurs only at higher temperatures. This unequivocally indicates that the H-D is an energy-limited process. Furthermore, however, in the case of Amberlite IR-120 the apparent exchange capacity measured at 90 C° is greater than at 71.5 C° (see below, with respect to Amberlite IRC-50), or a similar phenomenon is detected, such as is commonly known in connection with the activated adsorption of gases: the exchange capacity increases with an increase in temperature. At the same time, however, the dissociation of deuterium oxide also increases, and the diffusion of deuterium-containing hydroxonium ions within the resin is speeded up, and thus a greater speed of exchange may be expected. This increase in speed was actually observed in the case of both resins investigated (Table 3, Figure 2).

In the case of Amberlite IRC-50 less deuterium was bound at 90 C° than at 71.5 C°. The explanation of this behavior, which at first glance appears surprising, may be found in the fact that carboxylic resin is more sensitive to temperature, and beyond a certain, definite temperature, the number of active places is reduced. According to data contained in the literature³ both Amberlite IR-120 and Amberlite IRC-50 may be used up to 121 C°, which data, however, relate to resin in the form of sodium salt (Table 1).

The drop in the number of active places also was controlled through titration by determination of the total ion-exchange capacity of the resin at 20, 71.5, 80 and 90 C°. For Amberlite IR-120 the capacities measured at the four temperatures were identical, but for Amberlite IRC-50 the capacity at 80 and 90 C° was less than at 20 C° (Table 1).

If the deuterium mol fraction of the resin (X_{Dt}) is calculated at the lower capacity (m_{Ht}) of the experimental temperatures, the values obtained at 80 and 90 C° are greater than the value obtained at 71.5 C°.

Plotting the end values of exchange as a function of temperature (Figure 3), it is seen that the end quantity of Amberlite IR-120 increases with temperature, and the end value of Amberlite IRC-50 reaches a maximum at approximately 75 C°.

Plotting the end mol fractions as a function of temperature, we see that the X_D of Amberlite IRC-50 also has a maximum at approximately 75 C°, and its X_{Dt} increases with temperature.

The H-D Exchange Capacity as a Function of the p_H of the Solution

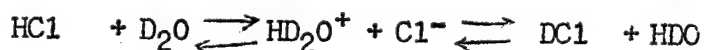
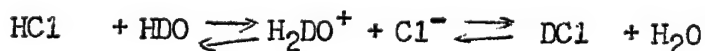
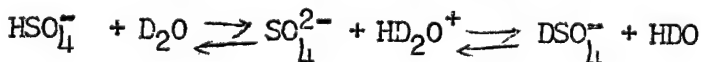
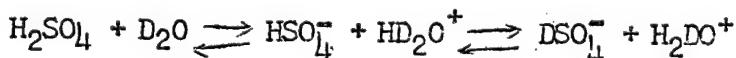
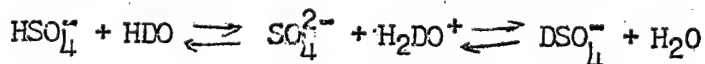
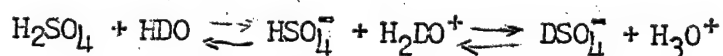
The change in hydrogen ion concentration in solution generally has two effects upon the cation exchangers: with a change in p_H the swelling of the resins, and the dissociation of the active groups change. According to data of the literature⁷ the ion exchange capacity of sulphonic acid resins generally is independent of the p_H of the

solution. [7 R. Griessbach: op. cit., page 233.] The cation exchangers swell more at a higher pH , whereupon the internal surface is more accessible to the particles. Because of the pH -dependence of swelling, in several cases the ion exchange capacity of the sulphonic acid resin to a slight extent may vary with the pH of the solution.⁷

In carboxylic resins the capacity increases with an increase in pH , not only because of greater swelling of the resin, but also because the exchange is a limited process and the number of dissociated carboxylic groups in the internal solution is determined by the pH of the solution⁶.

The deviation in the dissociation of the internal solution derives from the different acidity of the two resins. Determining the acidity of the ion exchangers through measurement of sugar inversion speed, the apparent acidity of sulphonic acid resin was found to be between that of hydrochloric acid and monochloroacetic acid, close to the latter. The acidity of carboxylic resins was found to be between that of formic acid and acetic acid.⁸ [8 Griessbach: op. cit., page 270.] Thus both the acidity investigations and study of the neutralization curves indicate that the sulphonic acid resins act like strong acids, and the carboxylic resins act like weak acids.

In deuterium-hydrogen exchange the hydrochloric acid or sulphuric acid added to solution for the purpose of reduction of the pH may have a role different from those described above. An exchange also takes place between the deuterium oxide and the two acids:⁹ [9 Zh. M. Serserer and A. I. Brodskiy: *Acta Fizikokhim.* URSS (Journal of Physical Chemistry), No 2, 1935, page 603.]



As a result of ionization and exchange the deuterium enters partially the hydrochloric acid and partially the sulphuric acid, or instead of deuterium oxide, which itself is only slightly soluble ($K_D 0 = 0.33 \cdot 10^{-14}$), the solution contains deuterium-containing ions.

Because of the greater deuterium ion concentration the end-point is reached more rapidly, and if the effect of the deuterio-acids is greater than the reduction of internal dissociation by the hydrogen ion concentration, the exchange capacity also may be altered.

An actually greater exchange capacity than that of sulphonic acid resin and more rapid attainment of end-point were obtained in deuterium oxide solution containing hydrochloric acid and sulphuric acid. With carboxylic acid, however, capacity drops with a reduction in pH , although the end-point also is reached more rapidly in this case (Table 4, Figures 4 and 6).

In Amberlite IR-120 the end concentration increases with a reduction in pH , and reaches saturation at $pH = 2.0$. The end values of sulphuric acid exchange are greater than that of hydrochloric acid (Figures 5(a) and 7 (a)).

In Amberlite IRC-50 the end values increase with an increase in pH . The end mol fractions vary linearly with the pH both in the presence of hydrochloric acid and sulphuric acid (Figures 5(b) and 7(b)).

Exchange Capacity as a Function of Resin Grain Size

Among others, diffusion of the exchanging ion within the resin has an important role in the exchanges which take place on the ion exchanger. Because with a reduction of the grain size of the resin the path of an ion from the surface of the resin to the active group within the resin is shortened, a greater reaction speed may be expected with a smaller resin diameter. For similar reasons the speed of reaction is greater in ester formation and hydrolysis catalyzed by cation exchangers if the radius of the ion exchanger is reduced.¹⁰ [10 J. Fodor and Z. Hajos: M. Tud Akad. VII. Oszt. Kozl. (Magyar Tudományok Akademiája VII. Osztály Közleményei — Reports of the Seventh Department of the Hungarian Academy of Sciences), No 5, 1955, page 545.]

According to our experiments (Table 6, Figure 8) the speed of exchange increases, and thus the end-point is reached more rapidly in both resins with a reduction in the grain size of the resin. The value of the deuterium concentration end point, however, is independent of the resin grain size, apparently because the active groups are evenly distributed on the resin.

TABLE 6

Exchange Capacity as a Function of Resin Grain Size
 Starting concentration 11.392 mol-% D₂ (Y₀); 2 g resin + 50 g
 solution; pH = 6.0; 71.5 Co
 (a) Amberlite IR-120

| Agita- tion Time | Decrease in Solution Con- centration, $\Delta Y_{+0.5}$ | | Decrease in Deuterium Con- tent of Solu- tion (ΔY) mol-% the Resin +0.0005 | | Quantity of Deuterium Bound on mckv/g (m _D) | | $X_D = \frac{m_D}{m_H}$ | | $X_D^* = \frac{m_D}{3m_H}$ | | a | | a ¹ |
|------------------------|--|------|--|--------|--|-------|-------------------------|-------|----------------------------|--------|-------|-------|----------------|
| | A | B | A | B | A | B | A | B | A | B | A | B | |
| 30 min | -- | 12.0 | -- | 0.0111 | -- | 0.304 | -- | 0.072 | -- | 0.0241 | | | |
| 1 hour | 7.9 | 15.4 | 0.0074 | 0.0143 | 0.202 | 0.392 | 0.048 | 0.093 | 0.0161 | 0.0311 | | | |
| 2 " | 15.1 | 17.7 | 0.0140 | 0.0164 | 0.384 | 0.449 | 0.091 | 0.107 | 0.0304 | 0.0356 | | | |
| 3 " | 17.9 | 17.8 | 0.0166 | 0.0165 | 0.455 | 0.452 | 0.108 | 0.107 | 0.0361 | 0.0359 | | | |
| 4 " | 17.8 | 18.0 | 0.0165 | 0.0167 | 0.452 | 0.458 | 0.107 | 0.109 | 0.0359 | 0.0363 | | | |
| 6 " | 18.0 | -- | 0.0167 | -- | 0.458 | -- | 0.109 | -- | 0.0363 | -- | 0.953 | 0.953 | 0.293 0.293 |
| | c | | c | | c | | c | | c | | c | | |
| 6 hours | 17.9 | | 0.0166 | | 0.455 | | 0.108 | | 0.0361 | | 0.946 | | 0.292 |

TABLE 6 (continued)

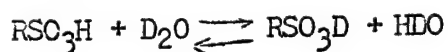
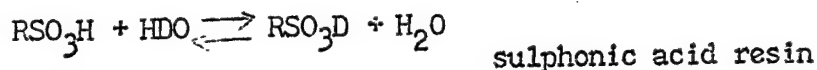
(b) Amberlite IRC-50

| Agitation Time | Decrease in Solution Concentration, ΔY | | | Decrease in Deuterium Content of Solution (ΔY) mol-% | | | Quantity of Deuterium Bound on the Resin (m_D) mckv/g | | | $X_D = \frac{m_D}{m_H}$ | | | a |
|----------------|--|------|------|--|--------|--------|---|-------|--------|-------------------------|--------|--------|-------------|
| | A | B | C | A | B | C | A | B | C | A | B | C | |
| 30 min | -- | 12.9 | -- | -- | 0.0120 | -- | -- | 0.329 | -- | -- | 0.0329 | -- | |
| 1 hour | 11.1 | 17.5 | -- | 0.0103 | 0.0162 | -- | 0.282 | 0.444 | 0.0282 | 0.444 | 0.0444 | -- | |
| 2 " | 21.7 | 23.9 | -- | 0.0201 | 0.0221 | -- | 0.551 | 0.606 | 0.0551 | 0.606 | 0.0606 | -- | |
| 3 " | 23.6 | 25.6 | -- | 0.0219 | 0.0237 | -- | 0.600 | 0.650 | 0.0600 | 0.650 | 0.0650 | -- | |
| 4 " | 25.2 | 25.6 | -- | 0.0233 | 0.0237 | -- | 0.639 | 0.650 | 0.0639 | 0.650 | 0.0650 | -- | |
| 6 " | 25.6 | -- | 25.6 | 0.0237 | -- | 0.0237 | 0.650 | -- | 0.650 | 0.0650 | -- | 0.0650 | 0.542 0.542 |

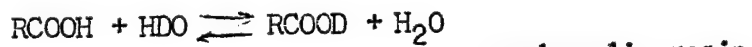
A $r_0 = 0.6$ to 0.45 mmB $r_0 = 0.4$ to 0.35 mmC $r_0 = 0.1$ to 0.06 mm

Evaluation

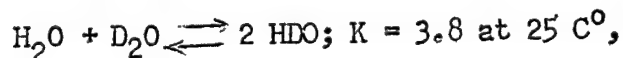
In the final analysis, the following exchanges take place between the cation exchangers and the deuterium oxide:



and



Because of the equilibrium between H_2O and D_2O ,



$$\text{and } K = 3.87 \text{ at } 100^\circ \text{C} \text{ [1]}$$

the ratio of HDO in the deuterium-content molecules was 0.939 in the 11.392 mol-% solution.

It is customary to give the degree of exchange in two different ways:

(a) Exchange is given only in reference to the resin, and the mol fraction (X_D) of deuterium bound on the resin is stated. The mol fraction is taken to mean the quantity of exchanged active places (m_D), divided by the quantity of the total active places on the resin (m_H).¹²
[¹² T. Erdőy-Gruz and G. Schay: Elméleti Fizikai Kémia (Theoretical Physical Chemistry), Vol II, page 394.]

(b) The exchange is indicated by the separation factor (a), which is in equilibrium with the deuterium/hydrogen ratio bound on the resin, and divided by the deuterium/hydrogen ratio present in solution.¹³

[¹³ D. R. Augood: *Nature*, No 178, 1956, page 754.]

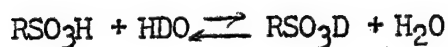
If the



exchange takes place, the separation factor is:

$$a = \frac{(I^2/I)A}{(I^2/I)B}$$

I represents the type of atom participating in the exchange, or the quantity of this atom (the hydrogen atoms of the resin), and I^2 represents the isotope which replaces the I atoms (deuterium). Only the quantity of exchangeable atoms was taken into consideration in the value of I (only those hydrogen atoms of the resin which are bound to the sulphonic acid or carboxyl groups). In the



and



exchanges:

$$\begin{aligned} \left(\frac{\text{I}^{\delta}}{\text{I}}\right)_A &= \frac{m_D}{m_H - m_D} = \frac{X_D}{1 - X_D} \quad \left(\frac{\text{I}^{\delta}}{\text{I}_B}\right) = \frac{Y_0 - \Delta Y}{100 - (Y_0 - \Delta Y)} \\ a &= \frac{\left(\frac{X_D}{1 - X_D}\right)}{\left(\frac{Y_0 - \Delta Y}{100 - (Y_0 - \Delta Y)}\right)} \end{aligned}$$

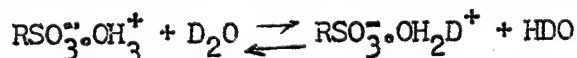
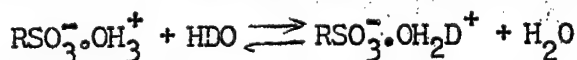
(Y_0 represents the starting concentration of deuterium in the solution, and ΔY represents the decrease in deuterium concentration of the solution in mol-%). The value of a is given in the last column of the tables.

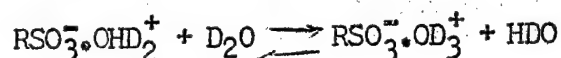
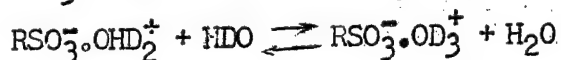
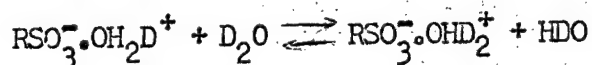
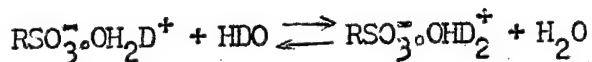
According to the data of the literature, in most cases a is very close to unity, which means that the distribution of isotopes is identical in both binding methods. Exceptions are the hydrogen-deuterium exchange between deuterium oxide and acetone ($a = 0.83$ to 0.71), ammonium chloride ($a = 1.25$), acetic acid ($a = 0.45$), sucrose ($a = 0.83$), pyrole ($a = 1.25$) and hydroquinone ($a = 0.884$), [14 A. I. Brodskiy: J. Phys. Chem. USSR, No 9, 1937, page 755.]

According to our experiments a always is less than unity for Amberlite IRC-50, and ranges between 0.96 and 1.42 for Amberlite IR-120.

The separation factor less than unity indicates that the hydrogen-deuterium exchange is a kinetically limited process because identical isotope distribution cannot be expressed in both phases. This also is indicated by the fact that the degree of exchange depends upon temperature. A similar phenomenon was found in exchange between naphthalene and DBr^{15} , in which a also depends upon the temperature: between 0°C and 70°C the separation factor changes from 0.32 to 0.41.

The $a > 1$ values encountered in a sulphonic acid resin probably are connected with the fact that because of the complete internal dissociation the exchange reactions are approximately the following:





From the equations it is clear that there are actually $3m_H$ exchangeable places on the sulphonic acid resin. Dividing the X_D values of the sulphonic acid resin by three (X_D^H), thus computing the value of a (a^H), in every case we get a value less than unity.

The probable reason for the fact that an actual equilibrium is not reached may be that the formation of the $\text{RSO}_3^-\text{OH}_3^+$ ion complex is a limited process. The ion-exchange resins contain bound water in various forms (structural, hydrate, or water of swelling). It is well known that the water absorption of a given resin also varies with the quality of the bound ion, because certain ions carry coatings of hydrate-water with them.

The sulphonic acid resins swell to a great extent, and the carboxylic resins swell to a slight extent. When the resin is dried out (air dry) part of the adsorbed water is removed, and this drying is partially an irreversible process, because the capacity to swell is reduced, active groups may break off, and the grain surface may be reduced, which phenomena cause a reduction in capacity.

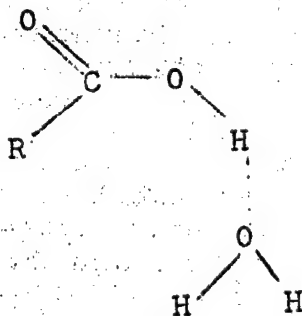
According to calculations the water remaining in the resin capillaries (approximately 20 percent) would be adequate to make $\text{RSO}_3^-\text{OH}_3^+$ ion-complexes from each RSO_3H group, but probably is inadequate to fill the capillaries with water and maintain the resin in a swollen condition. Because of this only part of the RSO_3H groups actually are in $\text{RSO}_3^-\text{OH}_3^+$ form originally. When the aqueous solution of deuterium oxide is added formation of the lacking $\text{RSO}_3^-\text{OH}_3^+$ groups begins, and this process is furthered by an increase in temperature.

In addition to the above, stereometric blocking also may occur in part of the active groups, and because of this the capacity is less than the value obtained by analysis of the finished resin.

The total ion-exchange capacity found in the literature³ is not an actual physical constant because it depends upon the quality of the ions, the swollen state of the ion-exchange resin, the previous history of the resin, etc. Thus the exchange capacity, established for an A-B ion-pair, is not definitely the same as for the A-C ion-pair, even though the previous history and swollen state of the resin may be identical. Thus the total ion-exchange capacity given in the literature for H-Na ion-pair may serve only for approximate orientation with respect to other ion exchanges.

A certain similarity may be found between the hydrogen-deuterium exchange and the isotope exchange in the case of hydrated polytungstenate in sulphonic acid exchangers. Spitsin and Berezhkina¹⁶ investigated the exchange between $\text{Na}_{10}\text{W}_{12}\text{O}_{41} \cdot 27.43 \text{ H}_2\text{O}$ and D_2O in a 2.3 mol-% deuterium oxide solution. [16 V. I. Spitsin and Kh. F. Berezhkina: Dokl. Akad. Nauk SSSR [Doklady Akademii Nauk — Reports of the Academy of Sciences USSR], No 108, 1956, page 1,088.] At 20 C° the exchange was rapid, and within 12 hours exchange was complete. At 100 C° the speed of exchange is more rapid. If the salt was partially dehydrated, for example if $\text{Na}_{10}\text{W}_{12}\text{O}_{41} \cdot 9.4 \text{ H}_2\text{O}$ were used, no exchange occurred at room temperature, but 2.7 H_2O was exchanged at 100 C°.

The situation is different with respect to carboxylic resin. Because of the low-dissociating COOH groups the $\text{COO}^- \cdot \text{OH}^+$ system cannot be formed, and thus a value of a greater than unity cannot be expected. The carboxylic resins, in contrast to the sulphonic acid resins, swell only slightly. The separation factor smaller than unity possibly may be explained by formation of hydrogen-bridges by the carboxylic resin with the aid of adhered water, similar to that of an aqueous solution of acetic acid:



The similarity of the two phenomena also is indicated by the interesting result that in exchange between acetic acid and an aqueous solution of deuterium oxide $a = 0.45$, in opposition to the value $a = 0.54$ obtained by us. According to the data of the literature a always is considerably less than unity¹⁴ in all hydrogen-deuterium exchanges in which weakly acidic groups participate in the exchange (phenol, acetic acid, etc.).

The next portion of our work will consist of investigation of hydrogen-deuterium exchange as a function of the deuterium content of the solution.

At this point the present author would like to express his thanks to Academician Geza Schay, the author's aspirant chief, who directed the work, to university professor Karoly Simonyi, who furthered the performance of the experiments with his advice, and to Mrs. Dezsone Trencseni, a technical associate of the author.

Summary

The replacement-exchange of hydrogen by deuterium on cation exchangers (Amberlite IR-120 and Amberlite IRC-50) was investigated in an aqueous solution of deuterium oxide as a function of the type of cation-exchange group, temperature, p_H of the solution, and grain size of the resin.

The speed of exchange and the final mol-fraction of deuterium is greater for the sulphonic acid resin than for the carboxylic resin, although the ion-exchange capacity of the carboxylic resin is greater.

At 20 C° there is no measurable exchange between deuterium oxide and the hydrogen atoms of the cation-exchangers, but it increases with temperature for Amberlite IR-120, and increases with temperature for Amberlite IRC-50 to approximately 75 C°, after which the amount of exchanged deuterium decreases because of damage to the resin. In both resins the speed of exchange increases with increase in temperature.

When the p_H of the deuterium oxide is modified through the addition of hydrochloric acid and sulphuric acid, the final exchanged quantity in Amberlite IR-120 increases with the decrease in p_H because of the exchange reactions between hydrochloric or sulphuric acid and the deuterium oxide. In Amberlite IRC-50 the exchange capacity decreases with the decrease in p_H , because under these circumstances dissociation of the carboxylic groups is suppressed. In both resins, however, the speed of exchange is greater in an acidic solution than in a neutral solution.

The exchange reaction speed increases with reduction of the grain size of the resin because of the reduced role played in the exchange by diffusion. The end concentration of deuterium on the resin, however, is independent of the grain size of the resin, probably because the active places are evenly distributed on the resin.

In the case of the carboxylic resin the separation factor always is smaller than unity, possibly because of hydrogen bridges formed between the carboxyl groups of the resin and the adhered water. The same occurs in the case of the acetic acid - deuterium oxide pair.

An increasingly larger apparent separation factor also was found for the sulphonic acid resin, which may be explained by the formation of $RSO_3^- \cdot OH^+$ ion-complexes by part of the RSO_3H groups. The formation of these ion-complexes, however, is a limited process which is aided by an increase in temperatures.

FIGURE APPENDIX

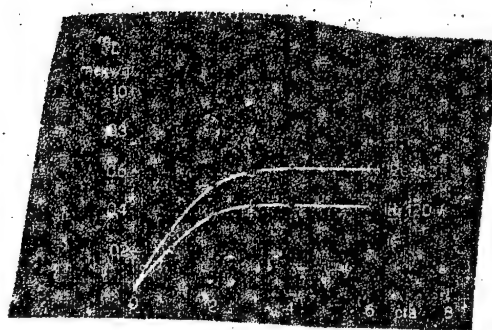


Figure 1. Exchange capacity as a function of the type of resin.

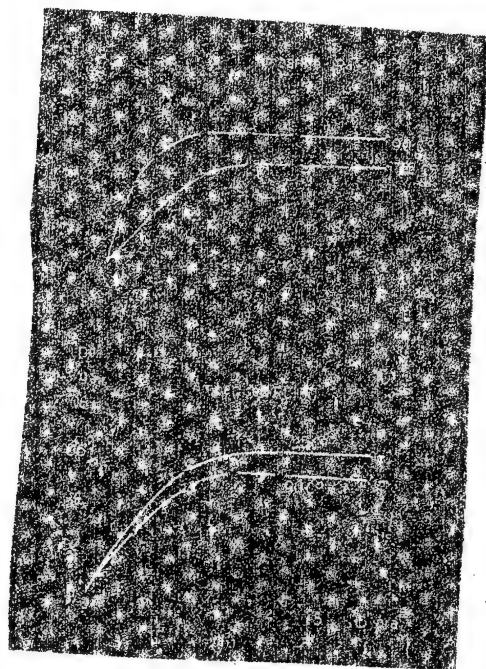


Figure 2. Exchange capacity as a function of temperature.

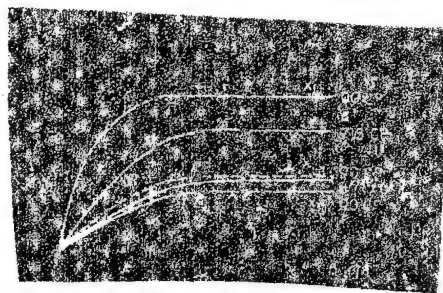


Figure 2(c). Mol-fraction of deuterium bound on the resin as a function of temperature.

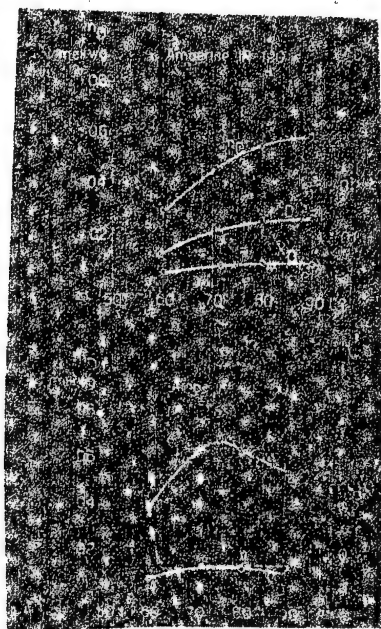


Figure 3. End exchange capacity and the end mol-fraction as functions of temperature.

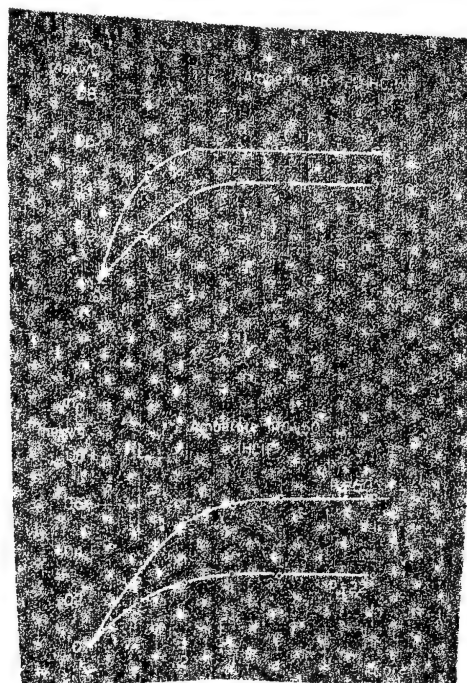


Figure 4. Exchange capacity as a function of pH of the solution when the pH is modified with hydrochloric acid.

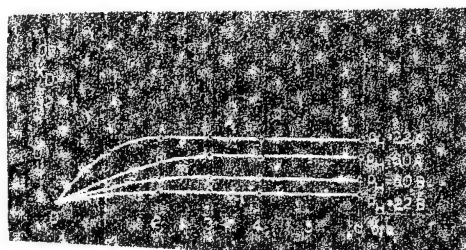


Figure 4(c). Mol-fraction of deuterium bound on the resin as a function of pH of the solution in the case of hydrochloric acid.

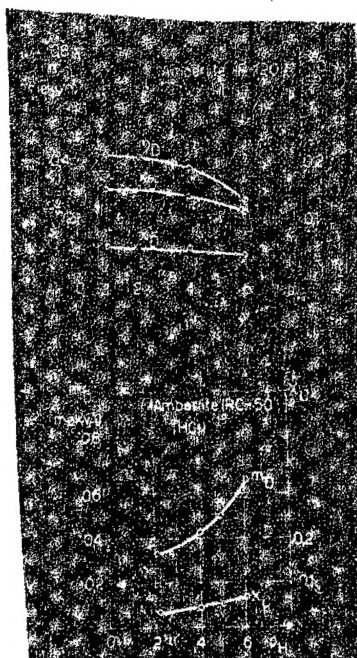


Figure 5. End exchange capacity and the end mol-fraction as functions of pH of the solution in the case of hydrochloric acid.

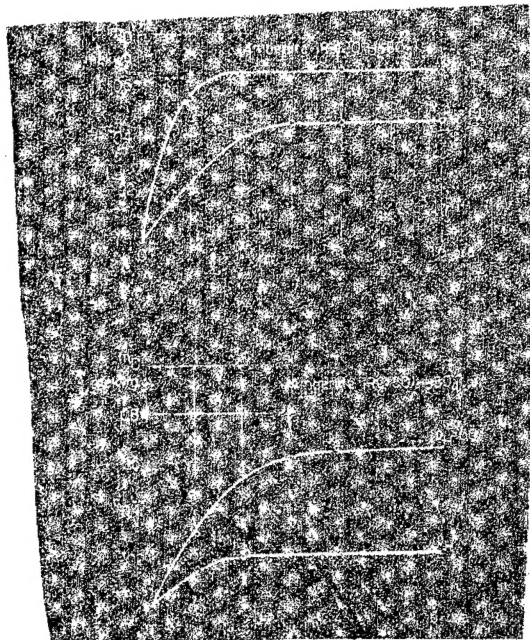


Figure 6. Exchange capacity as a function of p_H of the solution when the p_H is modified with sulphuric acid.

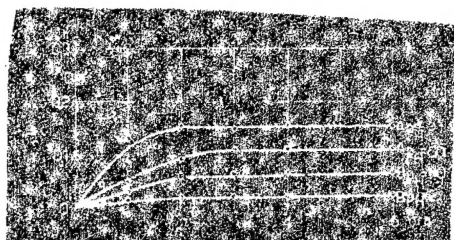


Figure 6(c). Mol-fraction of deuterium bound on the resin as a function of p_H of the solution in the case of sulphuric acid.

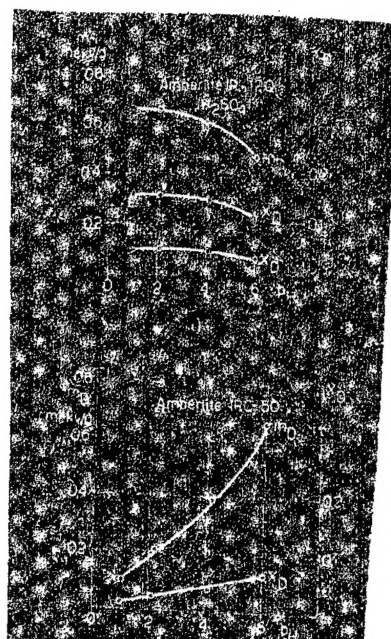


Figure 7. End exchange capacity and end mol-fraction as functions of pH of the solution in the case of sulphuric acid.

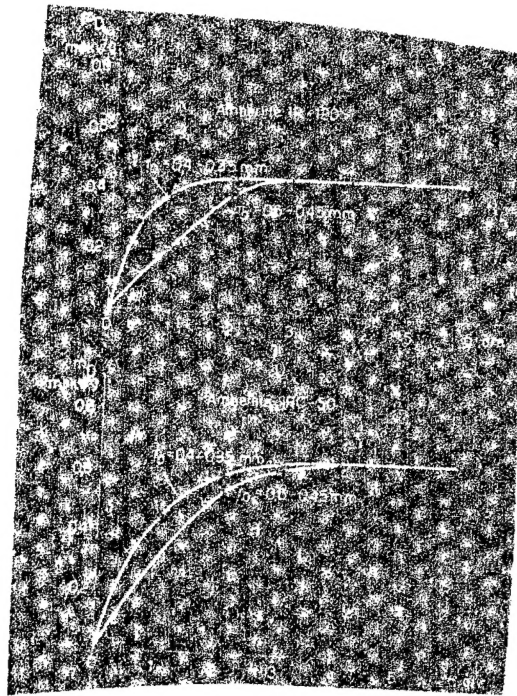


Figure 8. Exchange capacity as a function of grains size of the resin.

5200

END